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RESEARCH ON THE SAMARIUM-TYPE INTERMEDIATE
PHASES OF INTRA-RARE-EARTH BINARY SYSTEMS

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UNIVERSITY OF DENVER
DENVER RESEARCH INSTITUTE

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(Colorado Seminary)

RESEARCH ON THE SAMARIUM-TYPE INTERMEDIATE
PHASES OF INTRA-RARE-EARTH BINARY SYSTEMS

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ABSTRACT

The existence of a samarium-type phase in intra-rare-earth alloys, consisting of a light and a heavy rare earth, has been verified in the La-Gd, La-Y, Ce-Y, and Nd-Y systems. X-ray diffraction and metallographic techniques were employed to establish the composition limits of the single and two-phase regions. Precise lattice parameters and X-ray densities for the alloys were calculated from data obtained with the Debye-Scherrer camera. A hardness survey of the intra-rare-earth alloys is also presented.

I. INTRODUCTION

This Technical Report No. 1 is submitted in compliance with the terms of Contract No. Nonr-3661(02) between the Office of Naval Research and the Denver Research Institute, University of Denver. The report describes the progress made on the program entitled, "Research on the Samarium-Type Intermediate Phases of Intra-Rare-Earth Binary Systems." The period covered by this report is from 1 January 1962 to 31 December 1962.

The objective of this study is to investigate the alloying behavior and properties of intra-rare-earth binary combinations which display a singularly interesting phenomenon. This phenomenon is the formation of an intermediate phase with a samarium-type structure. The properties of the rare-earth components themselves and how they relate to the formation of the samarium-type structure are of parallel concern.

The rare-earth metals traditionally have been considered to be so similar in character that very little research on intra-alloying effects has been conducted. However, it is the feeling of the authors that such combinations offer a unique and interesting field of research with which to gain a better understanding of alloying behavior.

The anomalous formation of the samarium-type phase may in part be attributable to differences in crystal structure of the components. The light rare-earth elements - lanthanum, cerium, praseodymium, and neodymium - have a lanthanum-type (A$\frac{1}{4}$) hexagonal structure with a close-packed stacking sequence of ABAC, ABAC, etc. This structure has a double c-axis. The heavy rare earths - gadolinium, terbium, dysprosium, holmium, erbium, thulium, and lutetium - are of the magnesium or hexagonal close-packed type (A$_3$). Yttrium and scandium are included with this group because of the isomorphism. Samarium, on the other hand, crystallizes in a hexagonal type with a multiple c-axis or rhombohedral structure containing nine layers. The stacking sequence is ABABCBCAC, etc. This structure has been studied and established by Ellinger and Zachariasen[1] and Daane, et al.[2] The first work which indicated the presence of a similar samarium-type structure between intra-rare-earth combinations was reported recently by Lundin and Klodt[3] and Spedding, Valletta, and Daane[4]. Lundin and Klodt studied the Ce-Y system by metallographic techniques, finding the presence of an intermediate phase. Spedding et al. studied the La-Y and La-Gd

systems by metallographic, X-ray diffraction, and thermal analysis techniques. They established the existence of the samarium-type phase in these two systems.

In light of these studies, the hypothesis of this research work is that the criterion of formation of the samarium-type phase is to alloy a light rare earth with a heavy rare earth. It seems apparent that samarium metal is transition between the light and the heavy rare earths in crystal structure and other properties. Thus, if one obtains a transition phase isomorphous in structure with samarium metal on alloying a light and heavy rare earth, there may be a correlation between why it exists in these alloys and likewise in the series of lanthanon metals. If the samarium transition structure in the metals is stable because of size factor effects, it is conceivable that when one alloys a light rare earth with a heavy rare earth, an intermediate critical size factor is attained in the alloys wherein the more stable phase is samarium-type. It follows that the relative position of the intermediate phase in the binary system may be related to size effect. Since the interatomic distances throughout the lanthanon series are linear, the position of the intermediate phase would be approximated at a weighted average of the two components. These are only speculations, but they are speculations which require investigation. This phenomenon is one of the major features of interest in this program. Thus, a series of binary systems was selected to determine whether the criterion for the formation of the samarium phase is valid. The representative light and heavy rare earths of the binary systems are presented in Table I.

TABLE I

Intra-Rare-Earth Binary Systems

Light Rare-Earth Component	Heavy Rare-Earth Component
La*	Gd*
La*	Y*†
La	Ho
La	Lu
La	Sc†
Ce	Gd
Ce*	Y*
Ce	Ho
Ce	Lu
Ce	Sc
Nd	Gd
Nd*	Y*
Nd	Ho
Nd	Lu
Nd	Sc

* Indicates that the whole or partial phase diagram is available.
† These metals will be denoted as heavy rare earths in this study.

The systems were chosen on the basis of those components which are the extremes in atomic number in their respective group. For instance, in the light rare-earth group, lanthanum and neodymium are the extreme members. In the heavy rare-earth group, gadolinium and lutetium are the extreme members. Several intermediate members in each group are also represented. Yttrium and scandium are included because they are similar to the heavy rare earths but are grossly different in electronic structure and atomic diameter, respectively. Cerium has been chosen as an intermediate from the light rare-earth group, because it stands out with some rather significant differences in allotropy compared to the other light rare earths.

In the first year's study, progress is reported on four of these systems; I Gd, La-Y, Ce-Y, and Nd-Y. These four were chosen for the first year's study because some work has been reported for each.

Thus, establishing the difficult handling techniques on rare-earth systems where some data are presently available would aid in the further phases where the systems will be completely unknown. Metallographic, X-ray diffraction, hardness, and density data were obtained on these systems with the objective in mind of establishing the character of the samarium-type phase.

II.   EXPERIMENTAL PROCEDURES

A.   Materials

Of the rare-earth metals required for the conduct of this research, lanthanum, cerium, neodymium, samarium, gadolinium, holmium, and yttrium have been procured to date. These materials are sufficient to carry out the research on most of the binary systems that were proposed except those containing scandium and lutetium. The scandium and lutetium will be purchased at a later date after the investigations of the other binary systems have been essentially completed. The lanthanum, neodymium, gadolinium, and holmium were procured from the Lunex Company, the cerium from the Reno Metallurgy Research Center of the Bureau of Mines, and the samarium and yttrium from the Ames Laboratory. Table II presents the chemical analyses of these rare-earth metals.

TABLE II

Analyses of Rare-Earth Metals

Element	Lanthanum	Cerium	Neodymium	Samarium	Gadolinium	Yttrium	Holmium
O_2	510 ppm	60 ppm	140 ppm	- - -	210 ppm	2175 ppm	125 ppm
N_2	2	- -	6	$<$ 25 ppm	- -	90	- -
C	- -	500	- -	30	- -	- -	- -
Other Rare-earths	330	- -	50	≤ 400	325	330	110
Si	50	30	- -	- -	- -	200	- -
Fe	- -	220	- -	20	- -	108	- -
Mn	- -	- -	- -	- -	- -	- -	- -
Mg	50	- -	- -	- -	50	25	- -
Al	1	140	- -	- -	1	10	- -
Ta	10	- -	1	- -	10	60	- -
Ni	1	- -	1	- -	1	60	- -
Cu	1	50	10	- -	1	20	1
Ca	10	- -	1	500	1	10	10
Cr	1	- -	1	- -	1	20	1
V	- -	- -	1	- -	1	- -	1
B	- -	- -	50	- -	- -	3	- -
Nb	- -	- -	- -	- -	- -	- -	- -
Na	10	- -	10	- -	5	- -	- -
Be	1	- -	- -	- -	10	1	- -
K	1	- -	- -	- -	1	6	- -
Ti	1	- -	- -	- -	1	- -	- -
Co	1	- -	1	- -	1	- -	- -
Zn	50	- -	50	- -	50	- -	- -
Zr	20	- -	20	- -	20	3000	50
Cd	- -	- -	5	- -	- -	3	- -
Ce	50	99.87%	- -	- -	50	- -	- -
Mo	- -	200	- -	- -	- -	- -	- -
W	- -	40	- -	- -	- -	- -	- -

B.   Alloy Preparation

The as-received rare-earth metals were sectioned by hacksaw and cut with a jeweler's saw into small pieces suitable for weighing. These pieces were then filed with a clean file to obtain surfaces free from contamination. Clean tweezers were employed for all further handling after this stage of preparation. The charges for melting were prepared by weighing on an analytical balance to the nearest 0. 1 mg. Lanthanum and cerium charges, because of their reactivity, were cut and filed under an inert atmosphere in a dry box. Weighing was conducted rapidly, and the charges were placed immediately in the melting furnace which was subsequently evacuated. Exposure to air after cleaning and weighing was, therefore, kept to a minimum to prevent oxidation.

The melting was conducted under a slightly positive pressure of purified argon in a non-consumable electrode arc furnace. To ensure homogeneity the buttons of about 20g were inverted and remelted four times at 200 amp. The arc furnace and accessories are standard equipment, and the procedures have been described in the literature.

Weighing of the buttons after melting indicated negligible weight losses due to vaporization. Melting losses were consistently less than 0. 05 w/o.

Since no difficulties were experienced during the melting, and weight losses were negligible, no chemical analyses were deemed necessary. The nominal compositions of the buttons were selected on the basis of atomic percent. These buttons were then stored in a vacuum dessicator until required for further study.

C.   Heat Treatment

Metallographic examinations of the as-cast buttons revealed non-equilibrium microstructures which were difficult to interpret properly. It was therefore necessary to give these alloys a homo-genization treatment to restore equilibrium conditions. The alloy buttons were first wrapped in tantalum foil and then sealed in Vycor capsules under a partial pressure of argon. This tantalum foil served the dual purpose of providing protection to the specimen and physical support to the walls of the Vycor capsules. The capsules containing the samples were annealed in a resistance wound, vertical tube furnace. Furnace temperatures were maintained for

several hours at the desired level before the capsules were placed in the furnace. The temperature control was ±2°C of the desired temperature. At the conclusion of the anneals the specimens were cooled rapidly to retain the high-temperature structures.

The annealing temperatures and times are discussed in the following section.

D.   Metallography

The preparation of suitable surfaces of rare-earth metals or alloys for metallographic study is at best difficult. Two principal problems contribute to this difficulty. First of these is the attainment of a surface free of reaction products either from the etchant or air oxidation, and the second is a surface free from disturbed metal.

The metallographic specimens were first cut from the arc-cast button with a jeweler's saw to minimize heating and working of the alloy. This specimen was mounted in a cold-setting dental plastic not requiring heat and pressure for forming as does bakelite. Grinding was slowly carried out by hand with a solution of paraffin and Deobase (purified kerosene) as a lubricant and coolant. The grinding was done in stages with successive reductions in grit size, using 120, 240, 400, and 600 mesh papers in that order. A Syntron Vibratory Polisher, which polishes with a minimum of applied pressure, was employed for the polishing operation. The polishing was carried out in two stages. In the first stage, a slurry of Deobase and 5-micron alumina (Buehler AB#1) was used as a polishing medium with the Syntron operating at moderate amplitudes for $2\frac{1}{2}$ to 3 hours. The second stage of polishing was performed with a slurry of 0.3-micron alumina and Deobase. Synasol (denatured alcohol) was employed for rinsing between grinding and polishing stages, as water would react with the surface of the specimens.

A mixture of approximately three parts glycerol to one part of concentrated nitric acid was found suitable as a general etchant for all the rare-earth metals and alloys, with the exception of lanthanum-rich alloys. These require a milder etchant consisting of four to five parts of glycerol to one part of concentrated nitric acid. The etchant was applied by swabbing vigorously for 3 to 5 seconds with a saturated cotton swab. Immediate rinsing with profuse amounts of Synasol was employed to stop the etching action. The etchant is prepared fresh before each using, because it deteriorates in a few hours.

E.   X-Ray Diffraction

The powder method of X-ray diffraction was employed on all phases of the X-ray investigation.   Samples were reduced to powder by filing, and the powders were passed through a 325-mesh screen.   The screened powders were then packed into quartz capillary tubes having a uniform wall thickness of 0. 01 mm and an inside diameter of 0. 50 mm. It was necessary to perform all of the above procedures in an atmosphere of argon to eliminate oxide contamination of the powders.   The capillaries were then mounted on a vacuum manifold, purged, evacuated and sealed with an oxy-hydrogen torch.   The powder specimens were then annealed for 18 hr. at 300°C to relieve the cold work produced during filing.   Specimens prepared in this manner evidenced no oxide contamination during subsequent X-ray diffraction studies.

A 114. 6-mm diameter Debye-Scherrer camera was employed to determine the characteristic line patterns of the samples.   The camera was modified to retain a helium atmosphere during exposure. This modification permitted the use of a chromium target X-ray tube. The several advantages of employing chromium radiation in studying rare-earth alloy systems include the fact that none of the elements having atomic numbers ranging from 57 to 71 fluoresce when bombarded by characteristic chromium radiation.   The relatively long wavelength of chromium also produces maximum resolution of the characteristic line pattern of a crystalline material.

The data obtained from the Debye-Scherrer camera were employed for phase identification and also for calculation of precise lattice parameters and X-ray densities.   The unsymmetrical, or Straumanis, method of film loading was employed to provide correction factors for film shrinkage and unprecise camera dimension.   Line positions were measured to an accuracy of 0. 05 mm on a vernier scale illuminator. The film data were reduced on the Burrows 205 computer.   Input data consisted of 2S (theta in millimeters), which was read directly from the film, and the film shrinkage and camera radius correction factor. The computer internally calculated d-spacings, "Q" values, $\sin^2\theta$ and $\sin^2 2\theta$.   The Q (Q=1/d), $\sin^2\theta$ and $\sin^2 2\theta$ values were used to facilitate phase identification and line indexing.   Subsequent to phase identification precise lattice parameters for each phase present were determined.   Systematic and random errors in the parameter data were minimized by employing Cohen's least squares method[5], the solutions to Cohen's normal equations being obtained from the Burrows computer.

III.   RESULTS AND DISCUSSION

A.   Phase Equilibria

The nature of the research during the first year has been devoted to four intra-rare-earth binary systems. These are; La-Gd, La-Y, Ce-Y, and Nd-Y. Phase diagrams are available for three of these four systems; the Ce-Y,[3] La-Gd,[4] and La-Y[4] systems. Figures 1, 2, and 3 present the phase diagrams. These systems were chosen because experimental confirmation of the existence of the samarium-type intermediate phase has been established. Developing the necessary metallographic techniques to study their structures involved considerable expenditure of time and ingenuity because of their very reactive nature. Therefore, having some information already available on them aided in formulating and establishing procedures.

In all, sixty alloys were prepared by melting appropriately weighed charges under inert atmosphere in a non-consumable electrode arc furnace. This phase of the program required considerable effort because of the special handling techniques with the charge materials. Dry box procedures employing inert gas atmospheres were necessary to prevent surface contamination from the air. The details of the techniques of preparation have been described in a previous section. The range of alloys for each system was selected on the basis of the major structural features. Thus, the component metal solid solutions, the samarium-type intermediate phase, and the two-phase regions in between were included. The component metals-lanthanum, cerium, neodymium, gadolinium, and yttrium-were also arc melted and metallographically prepared. Their structures provided a base with which to compare the alloy solid solution structures. Table III lists the systems and the compositions prepared.

The nominal compositions that are presented in Table III represent close to actual compositions. Weight losses in arc melting were used as a guide to changes in the compositions of each button. The losses due to vaporization were consistently less than 0.05 w/o. Therefore, no chemical analyses were necessary because of the close tolerances maintained during arc melting.
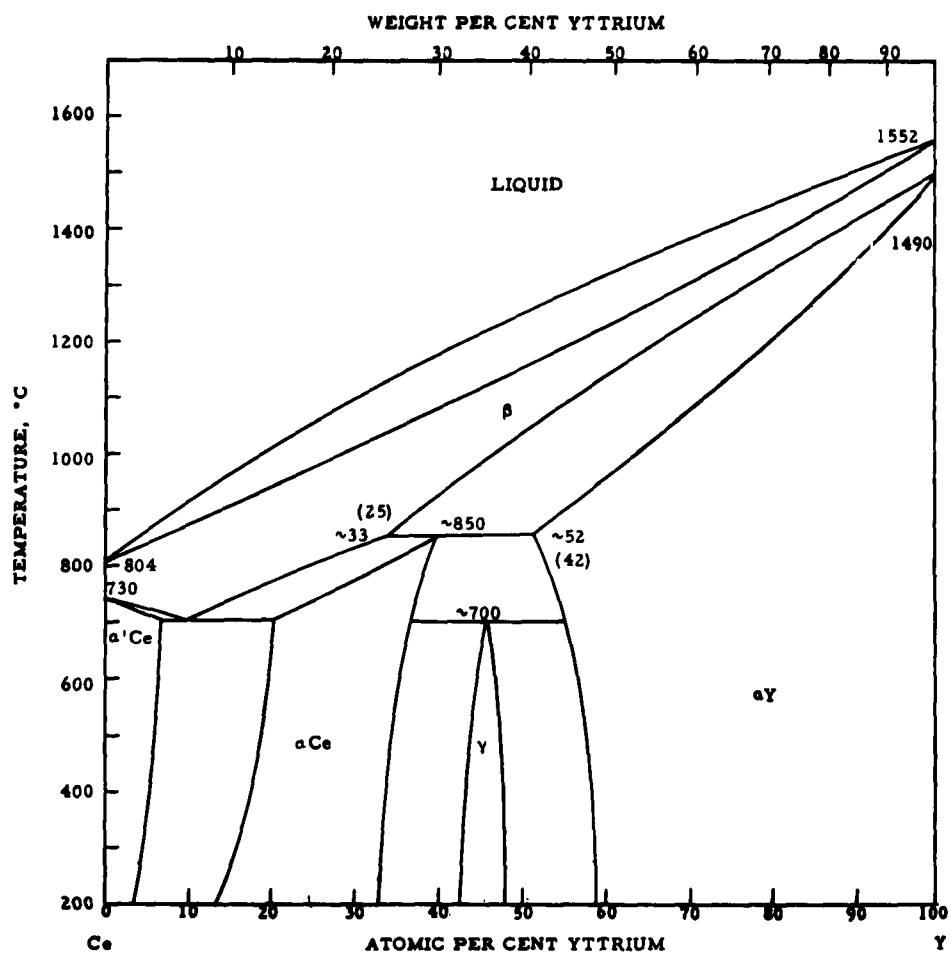
Figure 1. The Equilibrium Phase Diagram, Cerium-Yttrium[3]
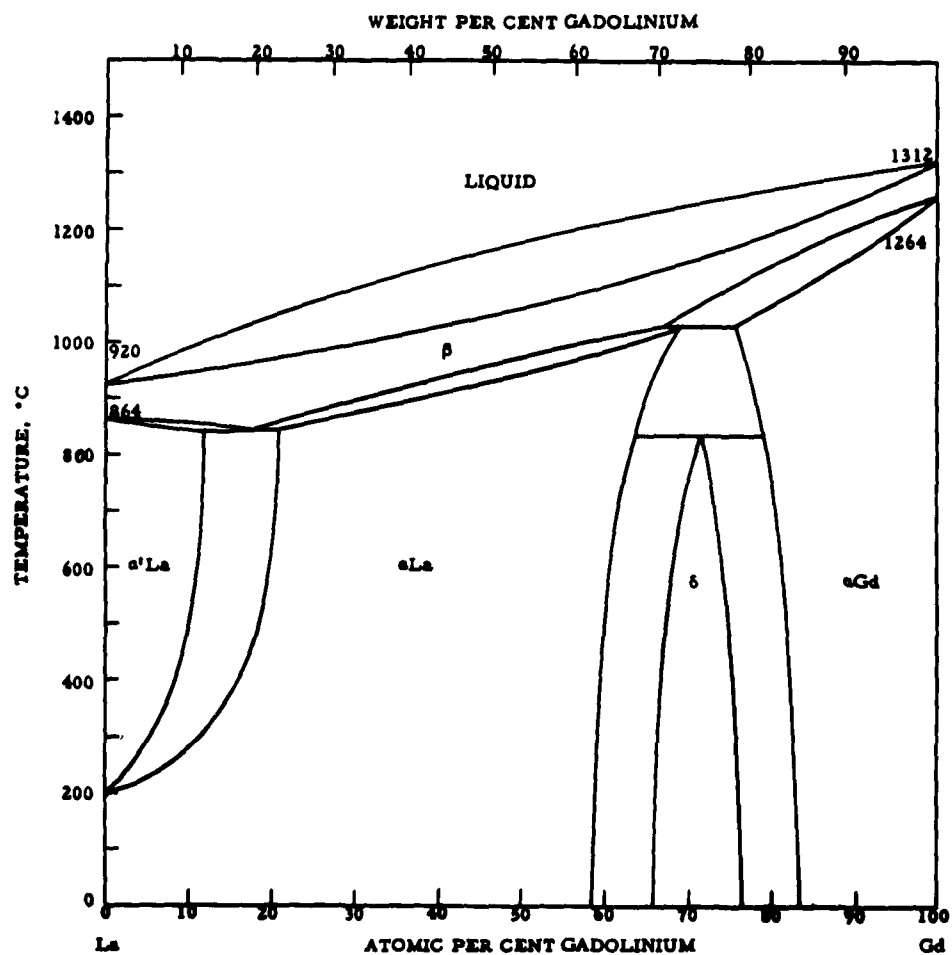
Figure 2. The Equilibrium Phase Diagram, Lanthanum-Gadolinium[4]
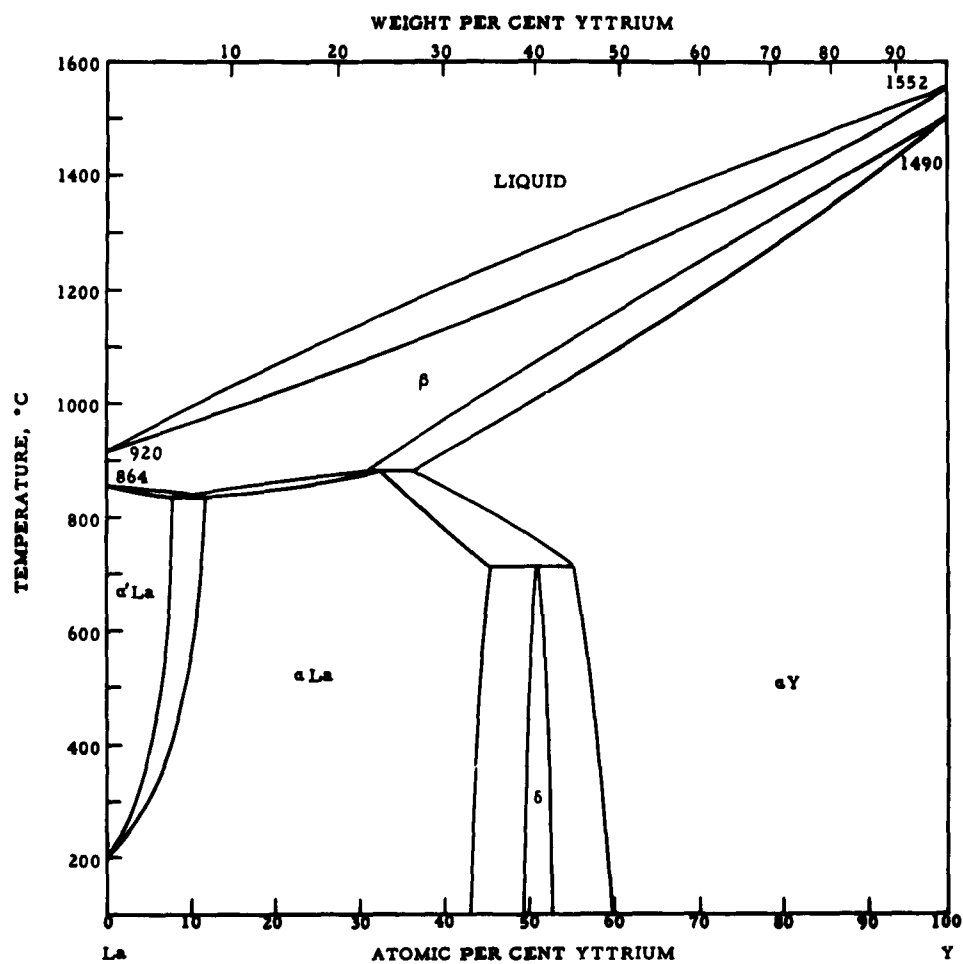
Figure 3.   The Equilibrium Phase Diagram, Lanthanum-Yttrium[4]

TABLE III

Intra-Rare-Earth Binary Alloys

Ce-Y		Nd-Y		La-Y		La-Gd	
a/o Ce	w/o Ce	a/o Nd	w/o Nd	a/o La	w/o La	a/o La	w/o La
30	21.9	40	52.0	20	28.1	10	8.9
35	26.0	45	57.0	36	46.8	12	10.8
40	30.1	50	61.9	38	48.9	14	12.6
45	34.2	55	66.5	40	51.1	16	14.4
50	38.8	60	70.9	42	53.1	18	16.2
55	43.3	65	75.1	44	55.1	20	18.1
60	48.4	69	78.4	46	47.1	22	20.1
65	54.0	70	79.1	48	59.1	24	21.8
70	59.3	75	83.0	50	61.0	26	23.7
75	65.1	80	86.7	52	62.9	28	25.6
		85	90.2	54	64.7	30	27.5
		90	93.6	56	66.5	32	29.4
		95	96.9	58	68.3	34	31.3
				60	70.1	36	33.2
				70	78.5	38	35.1
				80	86.2	40	37.1
						42	39.0
						44	41.0
						46	42.9
						50	46.9
						60	57.0

The metal components procured for this program were obtained from various sources in as pure a form as possible. The importance of low metallic impurities in the components used in phase diagram studies cannot be overly stressed. The analyses provided with each metal indicated overall purities as follows:

Lanthanum	> 99.8 w/o
Cerium	> 99.8 w/o
Neodymium	> 99.9 w/o
Gadolinium	> 99.9 w/o
Yttrium	> 99.5 w/o

Metallographic examination of both as-received and as-melted ingots showed evidence of oxide second phase which is clearly discernible in excess of the reported analysis. However, since the oxide phase remains essentially inert to the metallic equilibria, very little effect on the phase equilibria is expected. Singling out this impurity phase in the component metals and all of the alloys was not difficult, so it did not provide any problems such as masking the phase equilibria. The structures of the five rare-earth metals-lanthanum, cerium, neodymium, gadolinium, and yttrium-are presented in Figures 4 through 8, respectively. The lanthanum, cerium, and neodymium were particularly difficult to prepare to obtain a clearly defined microstructure. The problem was in maintaining a surface free of reaction product in the final stages of polishing and etching. These materials are extremely reactive. The minor phase which appears in all the metals at grain boundaries and within the grains is the oxide phase. At high magnifications it can be easily identified by its characteristic grey non-metallic appearance. It generally tends to follow crystallographic directions, as can be readily seen in the yttrium and gadolinium. Figure 9 is the structure of pure samarium metal which was obtained for comparison with the samarium-type intermediate phases found in the binary systems. The very fine striations and banding seen in the structure are very characteristic of the samarium-type phase in the alloys.

Very little metallographic analyses of the phase equilibria of the systems exist in the literature except for the Ce-Y[3] system, which was studied primarily by metallographic techniques. However, even in this system the region of the intermediate phase and the two-phase regions on either side were not clearly defined. A cursory metallographic study of the Nd-Y system was reported by Kirkpatrick ana Love[6]; however, these data are too preliminary to be meaningful. The sixty alloys prepared by arc melting were all subjected to metallographic analysis. On inspecting these samples by microscopic examination,
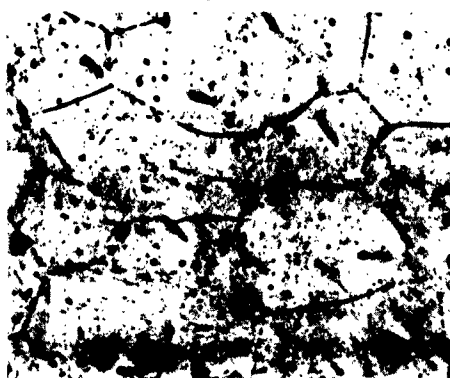
Figure 4.   The as-cast struc-
ture of lanthanum metal.
Impurity phase is oxide.
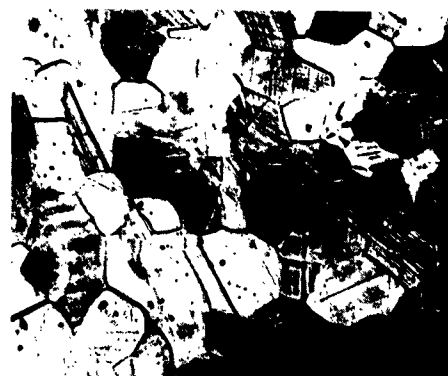
Figure 5.   The as-cast struc-
ture of cerium metal.
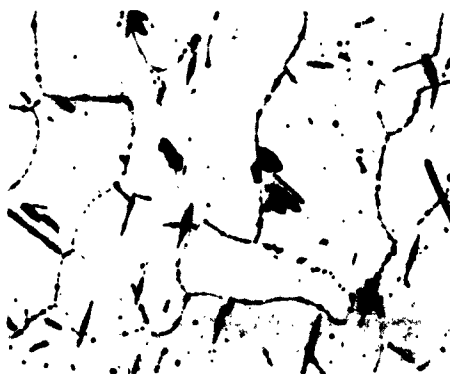
Figure 6.   The as-cast struc-
ture of neodymium metal.
Impurity phase is oxide.

Figure 7.   The as-cast struc-
ture of gadolinium metal.
Minor oxide phase present.

Figure 8. The as-cast struc-
ture of yttrium metal. Minor
phase is oxide.

Figure 9. The as-cast
structure of samarium
metal. Dark nodules are
oxide.

Figure 10. A 16 a/o
La-84-a/o Gd alloy. An-
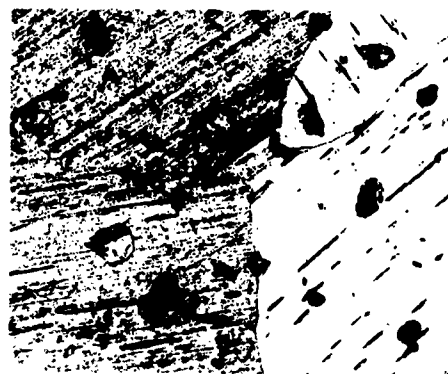nealed at 800C. Single-
phase gadolinium solid
solution.

Figure 11. An 18 a/o
La-82 a/o Gd alloy. An-
nealed at 800C. Two-phase
gadolinium solid solution
plus nucleating intermedi-
ate phase.

it was decided that high-temperature anneals were necessary. The as-cast structures were grossly non-equilibrium due to both coring during solidification and effects of transformation from the body-centered cubic form at the higher temperatures. Therefore, an annealing treatment was developed for all of the alloys to remove the inhomogeneities. It was decided to anneal at a temperature level just below the peritectoid reaction level in each system. The following schedule was then form-ulated to conduct the treatments:

System	Annealing Temperature, °C	Time, Hr
Ce-Y	650	150
La-Y	650	150
La-Gd	800	150
Nd-Y	650	150

The annealed structures were considerably more homogeneous; however, minor coring effects were noted in a few samples. These effects did not impair interpretation of the desired phase equilibria. The general characteristics of the four systems were so similar in structure that one system was selected to present the representative micro-structures in this report. The location of the terminal solid sol-ubility boundaries presented little difficulty because the change in micro-structure on entering the two-phase regions was definite. However, the single-phase, samarium-type structure was difficult to discern as to the width and exact location. The X-ray diffraction data provided a more accurate placement.

The La-Gd system was selected to represent the general struc-tural characteristics of the four intra-rare-earth binary systems. Starting from the gadolinium-rich end and moving in composition to the lanthanum-rich end of the system, the following microstructures are presented. Figure 10 is the structure of a 16 a/o La-84 a/o Gd alloy. The alloy is single phase with large equiaxed grains of the low-tempera-ture allotrope of gadolinium. The impurity phase in the form of the long stringers is the inert oxide phase. This alloy is very near to the terminal solid solubility limit. The next alloy, 18 a/o La-82 a/o Gd, shows that a two-phase region is present. Patches of second phase, the samarium-type structure, begin to appear. Figures 11 and 12 are the same alloy with different views. The transformed regions which have formed both at the solid solution grain boundaries and within the grains are separated by incoherent boundaries, indicating a major orientation

Figure 12. Another view of same alloy, showing larger patches of second phase. Note striations in second phase.

Figure 13. Same alloy under polarized light, showing a nodule of second phase. Nodule is made up of smaller areas with different orientations.

Figure 14. Same alloy, but another view of Figure 13. The microscope stage has been rotated to reverse the light intensities of the nodule.

Figure 15. A 28 a/o La-72 a/o Gd alloy representing the intermediate phase. Annealed at 800C. Note the striations throughout this phase.

difference between the matrix phase and the nucleating phase. It is
interesting to note the internal structure of the new phase. It is char-
acterized by extremely fine striations in the same direction in each
nodule. The striated phase can also be seen well under polarized light.
Figures 13 and 14 are photomicrographs of this alloy under polarized
light, showing a transformed patch consisting of many different impinged
orientations. The two views were taken with different rotations of the
stage. The reasons for this peculiar appearance have not yet been de-
termined, but several possibilities have been advanced. The striations
either have to do with the mode of transformation from the matrix, or
with changes occurring during the cooling from the annealing tempera-
ture. Further treatments at different times, temperatures, and rates
of cooling are contemplated to shed more light on this phenomenon.
These striations appear in similar form throughout the region where
the samarium-type phase occurs. However, it takes on somewhat dif-
ferent characteristics. The striations seem to become less diffuse and
fewer in number as the composition shifts to the light rare-earth solid
solution. In some cases rather broad bands of the samarium phase
exist. The possibility of these striations being a twinning phenomenon
due to metallographic working was considered. However, after con-
siderable experimentation with very careful polishing techniques, this
idea has been disproved. Figure 15 is representative of the structure
of the intermediate phase in a 28 a/o La-72 a/o Gd alloy. The stria-
tions in this structure have become less diffuse. X-ray diffraction
analysis of this alloy indicated that a completely single phase, samar-
ium-type structure exists. The photomicrograph of a 34 a/o La-66
a/o Gd alloy is shown in Figure 16. Rather broad bands of the struc-
ture now appear. The boundaries between adjacent grains are unique
in that they are extremely serrated. The appearance is suggestive of a
martensitic-type structure. X-ray diffraction analysis of this alloy
indicates that it is primarily the samarium phase with a minor amount
of the lanthanum solid solution. Figure 17 is the photomicrograph of a
36 a/o La-64 a/o Gd alloy showing a mixed structure. The banding still
appears. However, the alloy is approaching the single-phase region.
The structure presented in Figure 18 is of a 44 a/o La-56 a/o Gd alloy.
The alloy is single-phase lanthanum solid solution (A¹ type).

The interpretation of the microstructures of the annealed alloys
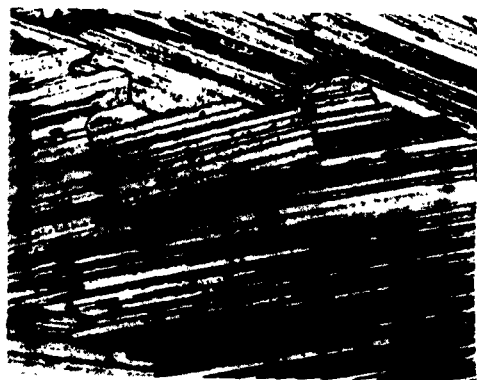are summarized in Table IV in which the phase boundaries are tabulated.

Figure 16. A 34 a/o La-
66 a/o Gd alloy, annealed
at 800C. Banding rather
prevalent.

Figure 17. A 36 a/o La-
64 a/o Gd alloy, annealed
at 800C. Two-phase
structure.
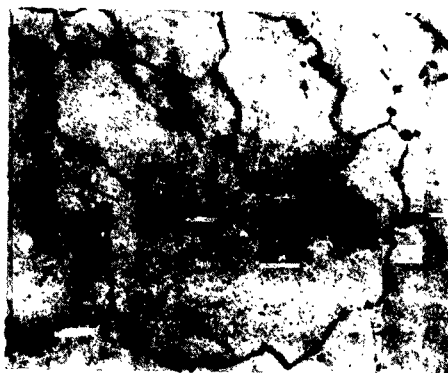
Figure 18. A 44 a/o La-
56 a/o Gd alloy, annealed
at 800C. Single-phase
lanthanum solid solution.

TABLE IV

Placement of Phase Boundaries

System	Light Rare Earth Terminal Solid Solution		Heavy Rare Earth Terminal Solid Solution		Intermediate Phase	
La-Gd	18	a/o La	~40	a/o La	~30	a/o La
La-Y	40	a/o La	~65	a/o La	~52	a/o La
Ce-Y	42	a/o Ce	~68	a/o Ce	~55	a/o Ce
Nd-Y	57.5	a/o Nd	~77.5	a/o Nd	~67.5	a/o Nd

In general, the heavy rare-earth terminal solid solubility was clearly defined. The light rare-earth terminal solid solubility boundaries were more difficult. In this region the structural changes are very subtle and seem to occur over a small range of composition as one moves from compositions in the two-phase field to the single-phase region. Placement of the position of the intermediate phase was even more difficult metallographically due to the very similar nature of the microstructures over a range of compositions. However, the X-ray diffraction data provide a much better fix on the position of this phase.

Hardness data were taken on selected alloys to determine whether the intermediate phase could be detected by distinctive trends. The pure metals were also subjected to hardness readings. These data are presented in Table V.

TABLE V

Hardness Data (10 kg, 10x)

Light Rare Earth	DPH	Intermediate Phase			DPH	Heavy Rare Earth	DPH
La	40	30	a/o La-70	a/o Gd	42	Gd	52
La	40	52	a/o La-48	a/o Y	55	Y	103
Ce	37	55	a/o Ce-45	a/o Y	47	Y	103
Nd	42	67.5	a/o Nd-32.5	a/o Y	41	Y	103

The hardness of pure samarium was determined to be 53 DPH which compares somewhat favorably with the intermediate phases. However, since hardness variations between identical samples varied by ± 5 DPH and the hardness change between the light rare earth component and the intermediate phase is small, very little basis for phase equilibria interpretation of these data is evident.

B.   X-Ray Diffraction

Preliminary to investigating the intermediate phases present in the four rare-earth alloy systems studied, the lattice parameters and densities of the pure constituents of these systems were determined. Optical metallographic examination of the pure materials in the as-received condition revealed the presence of a considerable volume of impurity. Subsequent to arc melting, however, metallographic examination revealed a considerable reduction in impurity content, and therefore the X-ray diffraction data obtained from the as-cast pure metals were regarded as the best available data in further considerations of the four alloy systems. In Table VI are listed the densities and lattice constants of the six metals investigated. For comparative purposes the lattice parameters of these materials, as determined by Herrmann, et al.,[7] are included.

In Tables VII through XI are listed the results of the X-ray diffraction studies of the Ce-Y, La-Y, La-Gd and Nd-Y alloy systems. Preliminary to preparation of X-ray specimens, the Ce-Y, La-Y, and Nd-Y alloys were equilibrated 150 hr at 650°C and the La-Gd alloys were equilibrated 150 hr at 800°C. X-ray specimens were exposed to filtered chromium K_α radiation for a period of 6 hr in the Debye-Scherrer camera. In most instances sharp diffraction patterns were obtained in which $alpha_1$, $alpha_2$ resolution occurred in the vicinity of 60 deg θ. No lattice parameters are reported for specimens which did not give good resolution in the back reflection region. All parameters given for the samarium phase are based on hexagonal indexing of the rhombohedral, $R\overline{3}m$ structure.

The Ce-Y system (see Table VII) exhibits alpha yttrium solid solution through 35 a/o cerium. The intermediate phase and alpha yttrium solid solution were found in samples containing from 40 through 46 a/o cerium. Alloys containing from 60 to 70 a/o cerium produced diffraction patterns which could not be interpreted completely by assuming that only the intermediate phase and the beta cerium solid solution were present. The alloy consisting of 75 a/o cerium in yttrium contained only the beta cerium structure. The unexplained complexity of the alloys containing 60 to 70 a/o cerium may be eliminated in future heat treatment studies.

TABLE VI

Lattice Constants and Densities of the Pure Intra-Rare-Earth Components and Samarium

Element	Pycnometric Density (gm/cm³)	X-Ray Density (gm/cm³)	Lattice Constants (Å)			Lattice Constants after Herrmann[7]		
			a_0	c_0	c/a	a_0	c_0	c/a
Ce	6.77	6.773	5.1600	---	---	5.1612	---	---
La	6.17	6.150	3.7767	12.1445	3.216	3.770	12.159	3.225
Nd	7.00	7.003	3.6609	11.788	3.220	3.6579	11.7992	3.226
Sm	7.50	7.572	3.6215	26.136	7.217	3.621	26.25	7.249
Gd	7.88	7.932	3.6285	5.7739	1.591	3.6360	5.7826	1.590
Y	4.49	4.491	3.6275	5.7688	1.590	3.6474	5.7306	1.571

TABLE VII

Lattice Constants and Densities of Cerium-Yttrium Alloys
Equilibrated 150 hr. @650°C

Composition a/o Ce	Pycnometric Density (gm/cm³)	X-Ray Density (gm/cm³)	Solid Solution Phase			Samarium Phase		
			a_o	c_o	c/a	a_o	c_o	c/a
30	5.15	5.202	3.6596	5.7397	1.568	--	--	--
35	5.28	5.246	3.6688	5.8015	1.581	--	--	--
40	5.36	--	3.6640	5.7854	1.580	3.6555	26.163	7.157
42	5.44	--	3.6692	5.7868	1.577	3.6588	26.159	7.149
44	5.48	--	3.6637	5.8182	1.588	3.6577	26.249	7.176
46	5.51	--	3.6688	5.8318	1.590	3.6607	26.280	7.179
50	5.65	5.621	--	--	--	3.6521	26.355	7.216
55	5.73	5.768	--	--	--	3.6446	26.368	7.235
60	5.83	--	Multiple phase materials. Films too complicated to permit interpretation					
64	5.94	--						
66	5.97	--						
68	6.02	--						
70	6.07	--						
75	6.19	6.214	3.6604	5.8582	1.600	--	--	--

TABLE VIII

Lattice Constants and Densities of Lanthanum-Yttrium Alloys
Equilibrated 150 hr. @650°C

Composition a/o La	Pycnometric Density (gm/cm³)	X-Ray Density (gm/cm³)	Solid Solution Phase a_o	c_o	c/a	Samarium Phase a_o	c_o	c/a
20	4.82	4.861	3.6640	5.8120	1.586	--	--	--
36	5.11	5.209	3.6859	5.8193	1.579	--	--	--
38	5.16	5.176	3.6928	5.8626	1.588	--	--	--
40	5.18	5.183	3.7058	5.8664	1.583	--	--	--
42	5.22	5.207	3.7021	5.9053	1.595	--	--	--
44	5.26	5.243	3.7063	5.9047	1.593	--	--	--
46	5.29	5.305	3.7016	5.9040	1.595	--	--	--
48	5.34	--	Poor resolution in back reflection region, 2 phases present					
50	5.37	5.382	--	--	--	3.7057	26.595	7.177
52	5.42	5.427	--	--	--	3.7045	26.624	7.187
54	5.43	--	Multiple phase material. Films indicate that alpha, beta and gamma lanthanum structures are present. Films too complicated to permit full interpretation.					
56	5.46	--						
58	5.49	--						
60	5.50	--						
70	5.68	--						
80	5.86	--						

TABLE IX

Lattice Constants and Densities of Lanthanum-Gadolinium Alloys
Equilibrated 150 hr. @ 800°C

Composition a/o La	Pycnometric Density (gm/cm³)	X-Ray Density (gm/cm³)	Solid Solution Phase			Samarium Phase		
			a_o	c_o	c/a	a_o	c_o	c/a
10	7.71	7.714	3.6426	5.8100	1.597	--	--	--
12	7.66	7.677	3.6482	5.8071	1.592	--	--	--
14	7.62	7.637	3.6513	5.8139	1.592	--	--	--
16	7.67	7.598	3.6540	5.8215	1.593	--	--	--
18	7.64	7.568	3.6545	5.8292	1.595	--	--	--
20	7.56	7.550	3.6534	5.8326	1.596	--	--	--
22	7.50	7.494	3.6557	5.8552	1.602	--	--	--
24	7.46	--	3.6531	5.8416	1.599	3.6498	26.106	7.153
26	7.43	--	3.6563	5.8549	1.601	3.6536	26.362	7.215
28	7.40	--	3.6342	5.8619	1.613	3.6589	26.446	7.228
30	7.34	7.363	--	--	--	3.6623	26.471	7.228
32	7.31	7.326	--	--	--	3.6638	26.518	7.238
34	7.27	7.286	--	--	--	3.6693	26.521	7.228
36	7.26	7.262	trace of 2nd phase present			3.6677	26.571	7.245
38	7.22	7.237	trace of 2nd phase present			3.6681	26.593	7.250
40	7.18	--						
42	7.16	--						
44	7.09	--						
46	7.07	--						
50	7.00	--						
60	6.82	--						

Multiple phase materials. Films indicate that alpha, beta and gamma lanthanum structures are present. Films too complicated to permit full interpretation.

TABLE X

Lattice Constants and Densities of Nd-Y Alloys
Equilibrated 150 hr. @ 650°C

Composition a/o Nd	Pycnometric Density (gm/cm³)	X-Ray Density (gm/cm³)	Solid Solution Phase			Samarium Phase		
			a_o	c_o	c/a	a_o	c_o	c/a
40	5.48	5.510	3.6645	5.7562	1.571	--	--	--
45	5.60	5.622	3.6680	5.7702	1.573	--	--	--
50	5.72	5.760	3.6679	5.7692	1.573	--	--	--
55	5.88	5.895	3.6666	5.7758	1.575	--	--	--
60	6.01	--	trace of second phase present			3.6466	26.316	7.217
65	6.14	6.228	--	--	--	3.6153	26.160	7.236
69	6.24	--	Poor resolution in back-reflection region, single phase					
70	6.27	6.246	--	--	--	3.6476	26.393	7.236
75	6.41	--	3.5251	11.6473	3.304	3.6277	26.318	7.255
80	6.54	--	Multiple phase material. Too complicated for interpretation					
85	6.66	6.734	3.6278	11.764	3.243	--	--	--
90	6.77	--	Poor resolution in back-reflection region, single phase					
95	6.89	6.934	3.6439	11.791	3.236	--	--	--

Alloys in the La-Y system (Table VIII) contain alpha yttrium solid solution through 46 a/o lanthanum and the intermediate phase in 50 and 52 a/o lanthanum alloys. Only one alloy, 48 a/o lanthanum in yttrium, was found to exhibit both of these phases. Specimens containing in excess of 52 a/o lanthanum were evidently nonequilibrium structures. These alloys contained the alpha, beta and gamma forms of lanthanum in addition to the intermediate phase.

In the La-Gd system (Table IX) the alpha gadolinium solid solution extends through 22 a/o lanthanum and the intermediate phase exists from 30 through 34 a/o lanthanum. These two phases coexist in alloys containing from 24 through 28 a/o lanthanum. The 36 and 38 a/o lanthanum alloys evidenced only a trace of second phase in addition to the intermediate phase. As in the La-Y system, thermal equilibrium was not attained in the lanthanum-rich alloys.

The intermediate phase occurs in the Nd-Y system (see Table X) at 65, 69 and 70 a/o neodymium, the alpha yttrium solid solution extending through 55 a/o neodymium. It will be noted that, although X-ray diffraction revealed the existence of alpha neodymium solid solution over a compositional range of 10 a/o, nevertheless one of the two alloys within the two-phase region containing the intermediate phase and neodymium solid solution exhibit diffraction patterns which are difficult to interpret.

In Table XIA are summarized the X-ray diffraction data for the intermediate samarium-type phases encountered in the four rare-earth alloy systems studied. Table XIB lists X-ray data recently published by Spedding, et al.,[4] for the intermediate phases in the identical alloy systems. The close correlation with respect to composition and lattice constants will be noted for the La-Ce, La-Y, and La-Gd alloys. However, in light of the present investigation it would appear that the data listed in Table XIB for the Nd-Y system is suspect.

TABLE XI

Lattice Constants of the Intermediate Phase Alloys Encountered in the Ce-Y, La-Y, La-Gd and Nd-Y Alloy Systems

A. Lattice Constants from Current Study

Composition	a_0 (A)	c_0 (A)	c/a
50 a/o Ce-50 a/o Y	3.6521	26.355	7.216
55 a/o Ce-45 a/o Y	3.6446	26.368	7.235
50 a/o La-50 a/o Y	3.7057	26.595	7.177
52 a/o La-48 a/o Y	3.7045	26.624	7.187
30 a/o La-70 a/o Gd	3.6623	26.471	7.228
32 a/o La-68 a/o Gd	3.6638	26.518	7.228
34 a/o La-66 a/o Gd	3.6693	26.521	7.238
65 a/o Nd-35 a/o Y	3.6153	26.160	7.236
70 a/o Nd-30 a/o Y	3.6476	26.393	7.236

B. Lattice Constants after Spedding, et al. [4]

Composition	a_0 (A)	c_0 (A)	c/a
44.5 a/o Ce-55.5 a/o Y	3.653	26.55	7.268
47.9 a/o La-52.1 a/o Y	3.699	26.70	7.218
30.1 a/o La-69.9 a/o Gd	3.667	26.482	7.222
53 a/o Nd-47.0 a/o Y	3.665	26.45	7.217

IV. FUTURE CONSIDERATIONS

During the next year the effort will be directed toward the study of the following five systems: La-Ho, Ce-Gd, Ce-Ho, Nd-Gd, and Nd-Ho. There are no data in the literature pertaining to the existence of the samarium-type intermediate phase in these five intra-rare-earth systems. The research of the previous year indicates that the composition of the samarium-type phase can be approximated on the basis of weighted averages of the interatomic distances of the components in the La-Gd, La-Y, Ce-Y, and Nd-Y systems. It is, therefore, reasonable to assume that the five new systems will also exhibit this behavior. Calculations based upon this premise indicate the following compositions for the occurrence of the samarium phase:

> La-Ho, 50 a/o La
> Ce-Gd, 25 a/o Ce
> Ce-Ho, 55 a/o Ce
> Nd-Gd, 50 a/o Nd
> Nd-Ho, 71 a/o Nd

Alloys on either side of these calculated compositions will be studied by X-ray diffraction and metallographic techniques to (a) establish whether or not the samarium phase does exist, and (b) to define the composition limits of the single and two-phase regions, if the samarium structure is found to occur.

ACKNOWLEDGEMENT

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